PATENT ABSTRACTS OF JAPAN

(11)Publication number : 60-226123
(43)Date of publication of application : 11.11.1985

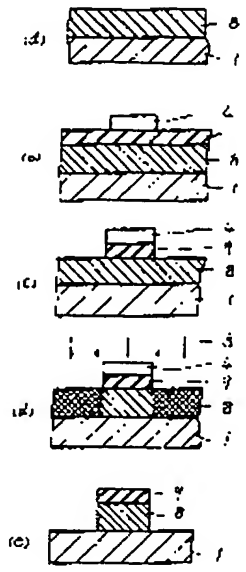
(51)Int.Cl. H01L 21/30
G03F 7/20

(21)Application number : 59-081994
(22)Date of filing : 25.04.1984

(71)Applicant : TOSHIBA CORP
(72)Inventor : NAKASE MAKOTO

(54) PATTERN FORMATION

(57)Abstract:
PURPOSE: To form a pattern with high patterning accuracy through etching with liquid by using a resist which is sensitive to radioactive ray for flattened layer, forming thereon a light shielding second film thereon, etching such film with a solution and executing development through exposure and transfer at a time with such etched film used as the mask.
CONSTITUTION: A material 1 to be etched, for example, SiO2 is coated with a resist PMMA sensitive to radioactive ray as the flattened layer 8, and it is then baked. As a film which shields the radioactive ray, Se, Ge 9 are deposited by the sputtering in the rate of 4:1. Thereafter, annealing is carried out, the surface is then coated with a positive resist and is baked. The surface is then exposed by a projection type exposing appratus and is developed with choline solution. A resist pattern 4 is thus formed. With the resist pattern 4 used as the mask, Se- Ge 9 is etched with an etchant obtained by adding Na2S into NaOH solution. Next, the entire part is irradiated with the far ultraviolet ray 5 in the wavelength of 260nm and a pattern is formed by developing the flattened layer 8 with methylisobutylketone organic solvent. Finally, SiO2 1 is etched with the flattened layer pattern 8 used as the mask.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLIPPEDIMAGE= JP360226123A

PAT-NO: JP360226123A

DOCUMENT-IDENTIFIER: JP 60226123 A

TITLE: PATTERN FORMATION

PUBN-DATE: November 11, 1985

INVENTOR-INFORMATION:
NAME
NAKASE, MAKOTO

ASSIGNEE-INFORMATION:
NAME COUNTRY
TOSHIBA CORP N/A

APPL-NO: JP59081994

APPL-DATE: April 25, 1984

INT-CL (IPC): H01L021/30;G03F007/20

US-CL-CURRENT: 250/475.2

ABSTRACT:

PURPOSE: To form a pattern with high patterning accuracy through etching with liquid by using a resist which is sensitive to radioactive ray for flattened layer, forming thereon a light shielding second film thereon, etching such film with a solution and executing development through exposure and transfer at a time with such etched film used as the mask.

CONSTITUTION: A material 1 to be etched, for example, SiO<SB>2</SB> is coated with a resist PMMA sensitive to radioactive ray as the flattened layer 8, and it is then baked. As a film which shields the radioactive ray, Se, Ge 9 are deposited by the sputtering in the rate of 4:1. Thereafter, annealing is carried out, the surface is then coated with a positive resist and is baked. The surface is then exposed by a projection type exposing appratus and is developed with choline solution. A resist pattern 4 is thus formed. With the resist pattern 4 used as the mask, Se- Ge 9 is etched with an etchant obtained by adding Na<SB>2</SB>S into NaOH solution. Next, the entire part is irradiated with the far ultraviolet ray 5 in the wavelength of 260nm and a pattern is formed by developing the flattened layer 8 with methylisobutylketone organic solvent. Finally, SiO<SB>2</SB> 1 is etched with the flattened layer pattern 8 used as the mask.

(19) Japan Patent Office (JP)

(12) **KOKAI TOKKYO KOHO (A)**
[OFFICIAL GAZETTE FOR UNEXAMINED PATENT APPLICATIONS]

(11) Japanese Patent Application Kokai Publication Number: **S60-226123**
(43) Publication Date: November 11, Showa 60 (1985)

(51) Int. Cl.[4]		Identification Code	JPO File No.
H 01 L	21/30		Z-6603-5F
G 03 F	7/20		7124-2H

Examination Requested: Not yet requested
Number of Claims: 1 (4 pages in total [in Japanese text])

(54) Title of the Invention: Pattern Forming Method

(21) Application Number: S59-81994
(22) Application Date: April 25, Showa 59 (1984)

(72) Inventor: Nakase, Makoto
c/o Kabushiki Kaisha Toshiba Sogo Kenkyujo
1 Komukai Toshiba-cho, Saiwai-ku, Kawasaki City,
Kanagawa Prefecture, Japan

(71) Applicant: Kabushiki Kaisha Toshiba
72-banchi Horikawa-cho, Saiwai-ku, Kawasaki City,
Kanagawa Prefecture, Japan

(74) Agent: Norichika, Kensuke, patent attorney, and one other

SPECIFICATION

1. TITLE OF THE INVENTION

Pattern Forming Method

2. SCOPE OF CLAIMS FOR PATENT

What is claimed is:

1. A pattern forming method for forming a mask pattern for etching during the manufacturing of semiconductor devices, comprising:

a process for applying a first coat of a radiation-sensitive resist on a semiconductor substrate having a material to be etched;

a process for forming a film having a light-shielding property against radiation on the resist film;

a process for applying a second coat of a radiation-sensitive resist on the light-shielding film;

a process for developing through exposure a desired pattern on the second film of radiation-sensitive resist and then for etching the light-shielding film using the pattern thus formed as a mask;

a process for creating on the first radiation-sensitive resist an exposed area, which corresponds to the pattern of the light-shielding film, by exposing all surfaces to radiation; and

a process for developing and forming a mask pattern for etching comprised of, at the least, the first radiation-sensitive resist.

2. A pattern forming method according to claim 1, wherein Se-Ge chalcogenide glass is used as the light-shielding film.

3. A pattern forming method according to claim 1, wherein a solution, which is obtained by adding Na_2S to an organic or inorganic alkaline solution, is used to etch the Se-Ge.

3. DETAILED DESCRIPTION OF THE INVENTION

Technical Field of the Invention

The present invention relates to a method for forming mask patterns used in the photo-etching process during the manufacturing of semiconductor devices.

Description of the Related Art and Problems

One example of a pattern forming method wherein a pattern is formed by laminating a number of layers is shown in FIG. 1. In the first place, in FIG. 1(a), a 2-μm flattened layer 2, for example, is deposited on a material to be etched 1, and then a transfer film 3, such as 2,000Å SiO_2 for example, is deposited thereon. Then, a photo-resist pattern 4 is formed, as shown in FIG. 1(b). The transfer film 3 is etched using the resist pattern as a mask, as shown in FIG. 1(c). Then, the flattened resist layer 2 is etched using the transfer film as a mask. Here, the positive-type resist is normally used for the flattened layer, and etching is performed by reactive ion etching using oxygen gas. In principle, it is desirable that the reactive ion etching is also employed to etch the transfer film. However, it is essential that reactive ion etching used to etch the flattened layer be of the anisotropic type in order to improve the accuracy of the

pattern. The problem with this was that expensive etching equipment was needed. There is another pattern formation method that is simple, does not require such equipment and uses two layers, as shown in FIG. 2. In FIG. 2(a), a coating of a radiation-sensitive resist, such as polymethyl methacrylate (PMMA), which is sensitive to far-ultraviolet light at the wavelength of 0.2 to 0.3 μm, is first applied as a flattened layer 2 on a material to be etched 1, and then a resist pattern 4 is formed thereon. Next, as shown in FIG. 2(b), the entire member is irradiated with far-ultraviolet light 5, in order to form an exposed part 6 and unexposed part 7 inside the PMMA of the flattened layer 2, using the resist pattern 4 as a mask. Next, as shown in FIG. 1(c), a resist pattern is formed by developing the flattened layer 2 with an organic solvent. Although the use of reactive ion etching equipment is not need with this method, an interstitial layer is often formed at the interface between the flattened layer 2 and the patterning resist 4. Consequently, this posed a problem so that, in order to avoid the formation of the interstitial layer, a separate layer of SiO_2 or other substance had to be provided between the two layers, resulting in a tri-layer string, or else ashing by oxygen plasma or some other procedure had to be performed before the flattened layer 2 was developed. Moreover, there was also a problem that the exposure wavelength range for each resist had to be varied in order to avoid subjecting the flattened layer 2 to exposure while the patterning resist 2 was being irradiated, and this resulted in a limitation placed on material selections.

Object of the Invention

The present invention is designed by taking into consideration the points described above and provides a new method for forming multi-layered patterns with high patterning precision and accuracy employing an ordinary wet-etching method without using reactive ion etching.

Summary of the Invention

The essential part of the present invention is that it provides a method for forming mask patterns having vertical side walls intended for use in etching. This is done by the use of a radiation-sensitive resist for a flattened layer and a second film of light-shielding material over this resist. The film is then etched and processed with a solution and then, using this as a mask, the entire member is exposed to light all at once to transfer and develop a mask pattern for etching having vertical side walls.

Description of the Preferred Embodiments

The present invention will be described in detail hereafter using examples.

(First Embodiment)

As shown in FIG.3(a), a 2 μm coating of radiation-sensitive resist PMMA was applied as a

flattened layer 8 to a material to be etched 1, such as SiO_2, and then baked at 180°C for one hour. Next, as shown in FIG. 3(b), a film of Se-Ge 9, in a ratio of 4:1, was deposited by sputtering to give a thickness of 2,000 Å. This served as a film having a light-shielding property against radiation. This was followed by annealing at 140°C for 30 minutes. A 1-μm coating of positive-type resist OFPR-800 was then applied, followed by 15 minutes of pre-baking at 90°C. The surface was then exposed to light by means of a projection-type exposure device and developed with a choline solution, in order to obtain a resist pattern 4. As shown in FIG. 3(c), the Se-Ge 9 was etched next with an etchant solution obtained by adding 1 mole of Na_2S to a NaOH solution using the resist pattern 4 as a mask. During this process, due to the mutually effective actions of the NaOH and Na_2S on the Se-Ge film, which has a columnar crystal structure, it was possible to obtain a Se-Ge film pattern that was accurate and with no undercut despite the fact that the etching was carried out with a solution. Next, as shown in FIG. 3(d), all surfaces were irradiated with 100 mJ/cm^{2*} of far-ultraviolet light 5 having a wavelength of 260 nm, and the flattened layer 8 was developed with a methyl isobutyl ketone organic solvent in order to form a pattern, as shown in FIG. 3(e). Finally, when SiO_2 1 was etched with a usual method and using the flattened layer pattern 8 as a mask, an SiO_2 pattern of high dimensional precision was obtained.

(Second Embodiment)

A pattern was formed using a 1-μm coating of negative-type resist OMR-83, which has a superior ability to resist alkali property, in place of the patterning resist OFPR-800 used in the first embodiment. All the steps used here after the patterning stage were the same as those of the first embodiment,

(Third Embodiment)

A pattern was formed using 2-μm thick positive-type resist OFPR-800 in place of the flattened radiation-sensitive resist PMMA of the first embodiment, and using an ultraviolet light with a wavelength of 400 nm from an ultra high pressure mercury lamp to irradiate all surfaces at once and developing with a choline solution. Besides these changes, all the steps used to form the pattern in this case were the same as those of the first embodiment.

(Fourth Embodiment)

A pattern was formed by depositing 200Å of Ag_2Se on the Se-Ge using electroless plating in place of the OFPR-800 used as a patterning resist of the first embodiment. Besides this change, all the steps used to form the pattern were the same as those of the first embodiment.

---

* Translator's note: Probable unit; the original text illegible.

In the present invention, the substance used as the radiation-sensitive resist, which forms each layer, should not be limited to those described in the above embodiments, and various other substances may be used to the extent that their use does not deviate from the aim of the present invention.

Advantages of the Invention

As described above, the present invention makes it possible to improve pattern accuracy by employing anisotropic etching, without using expensive etching equipment, and to solve the problem posed by the formation of an interstitial layer in between two radiation-sensitive layers.

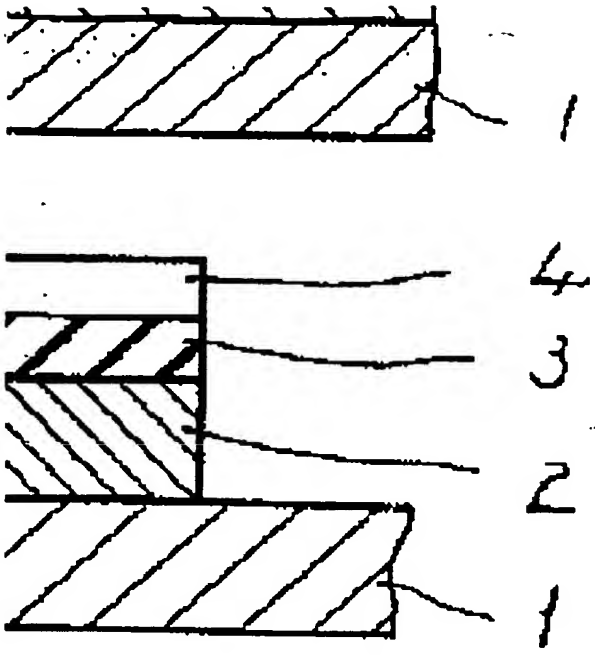
4. BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 and FIG. 2 are cross-sectional views illustrating existing pattern forming methods, while Fig. 3 is a cross-sectional view of processes illustrating an embodiment of the present invention.

Description of the Reference Numerals

1. Material to be etched
2. Flattened layer
3. Transfer film
4. Resist
5. Far-ultraviolet rays
6. Exposed part
7. Unexposed part
8. Flattened layer (PMMA)
9. Se-Ge film

Agent: Norichika, Kensuke, patent attorney (and one other)



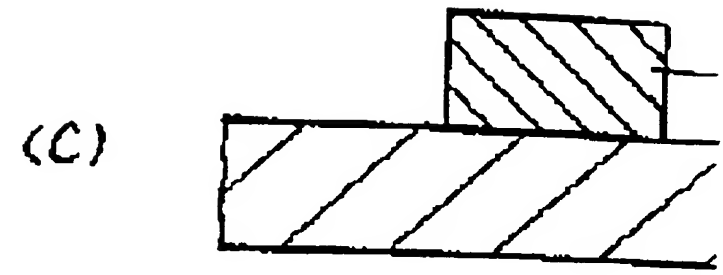
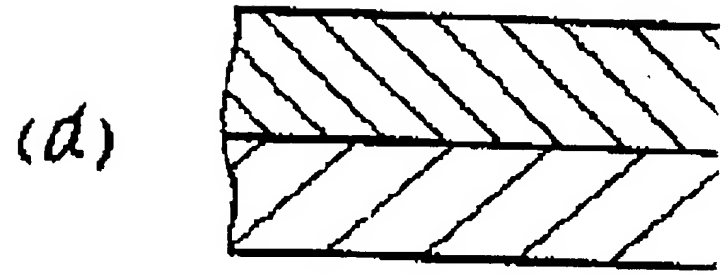
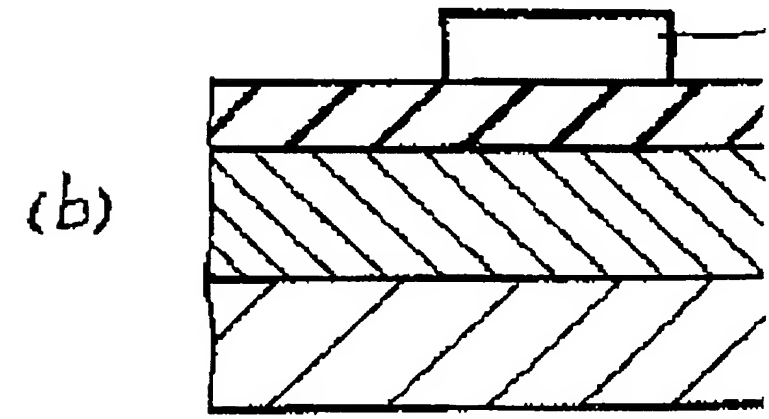
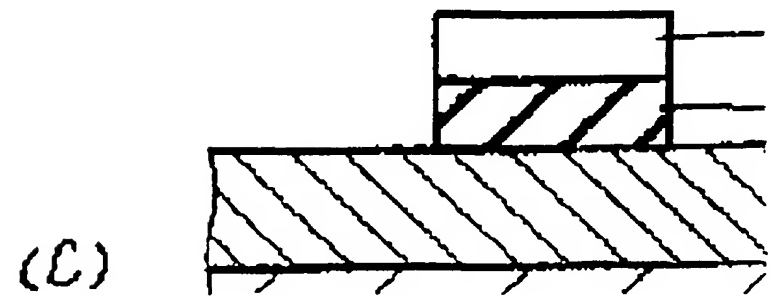


FIG. 3







⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭60－226123

⑤1Int.Cl.⁴	識別記号	庁内整理番号	⑬公開　昭和60年(1985)11月11日
H 01 L 21/30		Z－8603－5F	
G 03 F 7/20		7124－2H	

審査請求　未請求　発明の数 1　（全4頁）

⑭発明の名称　パターン形成方法

⑳特　願　昭59－81994
㉒出　願　昭59(1984)4月25日

㉑発明者　中瀬　真　川崎市幸区小向東芝町1　株式会社東芝総合研究所内
㉑出願人　株式会社東芝　川崎市幸区堀川町72番地
㉔代理人　弁理士　則近　憲佑　外1名

明　細　書

1. 発明の名称

パターン形成方法

2. 特許請求の範囲

(1)半導体装置の製造時の蝕刻用マスクパターンの形成において、被蝕刻材を有する半導体基板上に第1の放射線感応レジストを塗布する工程と、該レジスト膜上に放射線に対して遮光性を有する被膜を形成する工程と、該遮光性被膜上に第2の放射線感応レジストを塗布する工程と、該第2の放射線感応レジストに所望のパターンを露光現像し、これをマスクとして前記遮光性被膜を蝕刻する工程と、全面に放射線露光を行い、パターニングされた遮光性被膜に応じた露光領域を第一の放射線感応レジストに与える工程と、現像して少くとも第一の放射線感応レジストから成る蝕刻用マスクパターンを形成する工程を具備したことを特徴とするパターン形成方法。

(2)遮光性被膜にSe－Geカルコゲナイドガラスを用いることを特徴とする特許請求の範囲第1項記載のパターン形成方法。

(3)Se－Geの蝕刻に有機もしくは無機のアルカリ溶液にNa₂Sを添加した溶液を用いることを特徴とする特許請求の範囲第1項記載のパターン形成方法。

3. 発明の詳細な説明

〔発明の属する技術分野〕

この発明は、半導体装置の製造に於ける写真蝕刻工程のマスクパターンの形成方法に関する。

〔従来技術とその問題点〕

いくつかの層を積層してパターンを形成していく方法として、例えば第1図に示すようなものがある。まず第1図(a)に於いて、被蝕刻材1の上に例えば2μmの平坦化層2を、更にその上に例えば2000ÅのSiO₂トランスファー層3を積層させる。次に第1図(b)に示す様にフォトレジストのパターン4を形成する。その後第1図(c)に示す様にレジストパターンをマスクにしてトランスファー層3を蝕刻し、更に該トランスファー層をマスクにして平坦化レジスト層2を蝕刻する。この時の平坦

化層には通常ポジ型レジストが用いられ、その加工には酸素ガスを用いたリアクティブイオンエッチングが用いられる。トランスファー膜3の加工時にも原則的にリアクティブイオンエッチングを用いることが好ましい。しかしながら、この平坦化層の加工にはパターン精度を上げるため異方エッチングであるリアクティブイオンエッチングを用いることが必須である。そのために高価なエッチング装置を用いなければならないという問題があった。次に、このような設備を必要としない簡便な方法として第2図に示すような2層から成るパターン形成方法がある。第2図(a)に於いてまず被加工材1の上に放射線感応レジスト、例えば波長0.2～0.3μmの遠紫外光に感度を有するポリメチルメタクリレート（PMMA）を平坦化層2として塗布し、その上にレジストパターン4を形成する。次に第2図(b)に示す様に全面に遠紫外光5を照射し、平坦化層2のPMMA中にレジストパターン4をマスクとして露光部6と非露光部7を形成する。次に第1図(b)に示すように平坦化層2を有機溶剤にて現像し、レジストパターンを形成する。この方法ではリアクティブイオンエッチング装置を必要としないものの、平坦化層2とパターニングレジスト4との界面に介在層を形成することが多く、結局は介在層をさけるため、両層の間にSiO₂等の別の層を設けて3層のものとしたり平坦化層2の現像後に酸素プラズマによる灰化等を行わなければならないという問題があった。また、パターニングレジスト2への露光中の平坦化層2への感光を避けるため、各々のレジストの感光波長領域を異なるものとしたり、このため材料の選択に制限が生じるという問題があった。

（発明の目的）

本発明は上記の点に鑑みなされたもので、リアクティブイオンエッチングによらずに通常の溶液エッチングによりパターン精度のよいパターンを形成する新しい多層のパターン形成方法を提供するものである。

（発明の概要）

本発明の骨子は、平坦化層に放射線感応レジストを用い、その上に感光性の第2の膜を用い、該被膜を溶液により現像・加工後、これをマスクにして一括露光転写を行い、現像して垂直な側壁を有する被加工用マスクパターンを形成するものである。

（発明の実施例）

次に本発明の詳細を実施例を用いて説明する。

（実施例1）

まず、第3図(a)に示すように、被加工材1、例えばSiO₂の上に2μmの平坦化層8として、放射線感応レジストPMMAを塗布した後、180℃1時間のベーキングを行った。次に第3図(b)のように、放射線に対して感光性を具備した被膜としてSe₇₅Ge₂₅を4：1の割合でスパッタにより厚さ3000Åに被着させた。その後、140℃、30分のアニールを行った。更にその上にポジ型レジストOFPR800を1μm塗布し、90℃、15分のプレベーク後、投影露光装置にて露光し、コリン溶液にて現像してレジストパターン4を形成した。次に第3図(c)のごとく、レジストパターン4をマスクにしてNaOH溶液中に1モルのNa₂Sを添加した被加工液にてSe-Ge膜9を被加工した。この際、柱状結晶構造を取るSe-Ge膜にNaOHとNa₂Sが交互に有効に作用し、溶液による被加工にもかかわらず、アンダーカットのない精度のよいRe-Ge膜パターン9を得ることができた。次に第3図(d)に示すように、全面に波長260nmの遠紫外線5を、100mJ/cm²照射し、第3図(e)のように平坦化層8をメチルイソブチルケトン有機溶液にて現像しパターンを形成した。最後に平坦化層パターン8をマスクにして、SiO₂1を通常の方法で被加工したところ、寸法精度の良好なSiO₂パターンが得られた。

（実施例2）

実施例1のパターニングレジストOFPR-800のかわりに耐アルカリ性がより優れた、ネガ型レジストOMR83を1μm塗布し、パターニング後以下同様にしてパターン形成を行った。

（実施例3）

実施例1の平坦化放射線感応レジストPMMAに

かえて、厚さ2μmのポジ型レジストOFPR800を用い、全面一括露光用の光として超高圧水銀灯からの波長400nmの紫外光を照射し、現像をコリン溶液にて行い、以下同様の工程でパターン形成を行った。

〔実施例4〕

実施例1のパターニングレジストであるOFPR800にかえてSe-Ge上に200ÅのAg₂Se、無機界メッキにて被着させ、以下同様の工程にてパターン形成を行った。

本発明の各層を形成する放射線感応レジストは上記実施例に記載したものに限定されるものでなく、本発明の主旨を逸脱しない範囲で他のものを用いることができる。

〔発明の効果〕

以上述べたように本発明によれば、高価な縮小露光機を用いることなくして、非等方的な加工によりパターン精度を向上させることができ、又、2つの放射線感応層の間に形成される介在層の問題も解決することができる。

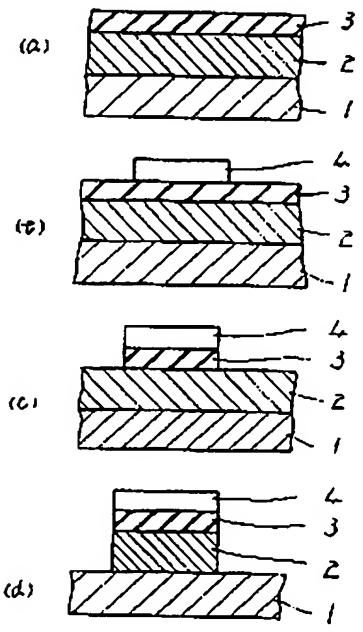
4. 図面の簡単な説明

第1図及び第2図は、従来のパターン形成方法を示す断面図、第3図は本発明の一実施例を説明するための工程断面図である。

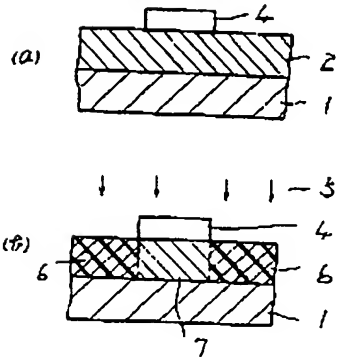
1…被加工材料、2…平坦化層、3…トランスファー層、4…レジスト、5…遠紫外光線、6…露光部、7…非露光部、8…平坦化層（PMMA）、9…Se-Ge層。

代理人 弁理士 則 近 憲 佑 （ほか1名）

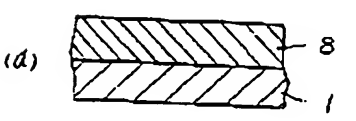
第 1 図



第 2 図



第 3 図



第 3 図